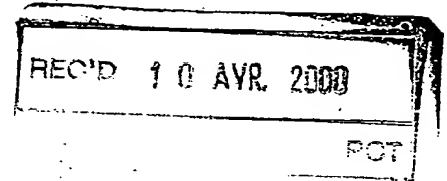




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I, ANNA MAIJA MADL, ACTING TEAM LEADER EXAMINATION
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Provisional specification in connection with Application No. PP 9413 for a
patent by THE UNIVERSITY OF MELBOURNE filed on 23 March 1999.



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A. M. Madl

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PROVISIONAL SPECIFICATION

FOR THE INVENTION ENTITLED:

"IMPROVED CARBON-CONTAINING MATERIALS"

Applicant:

THE UNIVERSITY OF MELBOURNE

IP Australia

Documents received on:

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Batch No:

Melbourne

The invention is described in the following statement:

IMPROVED CARBON-CONTAINING MATERIALS

The invention relates to improved carbon-containing materials, methods for their preparation and articles manufactured from them, in particular steel fabrication equipment, electrolytic cells used in aluminium production and other engineering products.

Carbon bonded composite materials are finding increasing use as replacements for traditional ceramic composites. Such replacement usually results in greatly improved properties and processing ability. Examples can be found in a wide range of industries which include those manufacturing refractory products such as steel fabrication equipment and electrolytic cells used in aluminium production.

In the preparation of carbon bonded composites, an organic polymer phase is converted to a type of carbon during heating which usually progresses through various temperatures of up to 2000°C. These composites also generally contain carbon black fillers which are added to control rheological properties, assist in processing or improve mechanical properties. The physical state of the carbon may vary from fine particles to fibers and platelets.

Although this practice has been adopted for many years, the effect of carbon black on the organic polymer phase formation during curing and the carbon structure produced during pyrolysis is not known. We have now found that carbon black has an enormous impact on the final formation of the carbon material from the polymer. In general, the porosity of the carbon material derived from polymer resin will increase when more carbon black is added. This porous structure results in low density and poor mechanical properties. We have also found that other carbon sources such as pulverized graphite or carbon derived from pyrolysis of phenolic resins exhibit similar effects to carbon black.

Mesophase carbon was developed in the last few years for the purpose of making graphitic carbon at relative low temperatures of 2000 to 2500°C. Mesophase carbon may be derived synthetically or from petroleum pitch. Synthetic mesophase which can be derived from aromatic hydrocarbons such as naphthalene consists of up

to 100% anisotropy, while mesophase derived from petroleum pitch usually has 75% anisotropy. Synthetic mesophase was developed as a superior precursor to graphitisation and is extensively used in carbon fiber applications. Such materials are usually used as a binderless mould and application temperatures are generally more
5 than 2000°C.

We have now found that when mesophase carbon is used as a filler in combination with an organic polymer that carbon materials having unexpected and improved properties are obtained. These carbon materials generally have a low porosity measured as a low surface area, high carbon yield, high composite density
10 and good mechanical properties.

According to one aspect of the present invention there is provided a composition suitable for the preparation of a carbon-containing material including:

- (i) a binder phase containing a polymer or a polymer composite; and
- (ii) mesophase carbon.

15 According to another aspect of the present invention there is provided a method for preparing a carbon-containing material including the steps of:

- (a) mixing a binder phase containing a polymer or polymer composite with mesophase carbon;
- (b) curing the mixture; and
- 20 (c) heating the cured mixture.

The term "polymer" is used herein in its broadest sense to denote low molecular weight polymerisable entities through to higher molecular weight entities containing many repeat units. The term includes dimers and oligomers.

Preferably, the polymer has at least one hydrogen bond. Examples include
25 polymers having hydroxyl, carbonyl, carboxyl, amine or thiol groups. Suitable polymers are those of the formulae (I) and (II) respectively:



wherein X is oxygen, sulphur or nitrogen and R is aryl, imidoaryl, alkyl, alkenyl, alkynyl or heterocyclyl which may be optionally substituted.

In this specification "optionally substituted" means a group that may or may not be further substituted with one or more groups selected from alkyl, alkenyl, alkynyl, aryl, halo, haloalkyl, haloalkenyl, haloalkynyl, haloaryl, hydroxy, alkoxy, alkenyloxy, alkynyloxy, aryloxy, carboxy, benzyloxy haloalkoxy, haloalkenyloxy, haloalkynyloxy, haloaryloxy, nitro, nitroalkyl, nitroalkenyl, nitroalkynyl, nitroaryl, nitroheterocyclyl, azido, amino, alkylamino, alkenylamino, alkynylamino, arylamino, benzylamino, acyl, alkenylacyl, alkynylacyl, arylacyl, acylamino, acyloxy, aldehydo, alkylsulphonyl, arylsulphonyl, alkylsulphonylamino, arylsulphonylamino, alkylsulphonyloxy, arylsulphonyloxy, heterocyclyl, heterocycloxy, heterocyclylamino, haloheterocyclyl, alkylsulphenyl, arylsulphenyl, carboalkoxy, carboaryloxy, mercapto, alkylthio, arylthio, acylthio and the like.

Polymers having hydroxyl groups such as those of the formulae (I) and (II) above wherein X is oxygen and R is optionally substituted aryl, for example, optionally substituted phenolic resins are preferred. Suitable phenolic resins include phenol-aldehyde type resins such as phenol-formaldehyde type resins, for example, resole or novolac and phenolic imide or phenolic polyimide. It will be appreciated that the phenolic resins may be substituted with any non-deleterious substituent including alkyl, for example, methyl or t-butyl; or imide, for example, maleimide or succinimide.

The term "polymer composite" is used herein in its broadest sense and refers to the combination of a polymer with another material, such as, for example, other polymers, particulate matter and/or additives known in the polymer art. It will be appreciated that one or more of the other materials may be inert or chemically reactive. The polymers may be selected from those defined above and can be in the form of dispersions, fibers or particles. Examples of particulate matter include coated or uncoated fibers, platelets, pigments, fillers, polyesters, metallic mesh, silicon oxides, graphite, carbon black, carbides or nitrides and inorganic material such as aluminium, magnesia, zirconia, bauxite, clay, alumina, TiB_2 or titanium oxide. The

additives may include crosslinkers such as hexamine which is also known as hexamethylene tetramine (HMTA), polymerisation promoters, catalysts, soaps, wetting agents, accelerators, hardeners and sources of formaldehyde such as formalin, paraform or trioxane. Suitable polymer composites include novolac-HMTA, novolac-furfuryl alcohol(FA)-HMTA, resole-novolac-HMTA, resole-carbon, resole-carbon-novolac-HMTA-FA, novolac-HMTA-FA-carbon, novolac-HMTA-FA-carbon-TiB₂, resole-carbon-alumina-silica, carbon-TiB₂-resole, imidophenol-HMTA, poly(N-(hydroxyphenyl) maleimides)-HMTA and polyimide-novolac. A preferred polymer composite is novolac-FA-HMTA.

10 The mesophase carbon can be in the form of fibers, pellets, platelets or powder. The powder form can be obtained by pulverising the mesophase in a ball mill. As discussed above, the mesophase may be derived synthetically from aromatic hydrocarbons such as naphthalene or from petroleum pitch. Examples include 100% anisotropic mesophase derived from naphthalene and 75% anisotropic mesophase
15 derived from petroleum pitch. The 100% anisotropic naphthalene may be prepared by cationic oligomerisation catalysed by HF/BF₃. The mesophase may be untreated or pre-treated by heating generally up to about 600°C.

The polymer or polymer composite and/or mesophase carbon may be presented in the form of a solution. The solvent used in the solution can be inert or
20 chemically reactive and may contribute to the properties of the polymer or polymer composite. It is often advantageous for the solvent to be incorporated in the polymer or polymer composite as it will not then require removal which may be difficult. This also reduces the loss of weight of the polymer or polymer composite on curing. The choice of solvent will depend on the type of polymer, polymer composite and/or
25 mesophase carbon employed. Suitable solvents include water or organic solvents such as aromatics, for example, toluene or benzene; ketones, for example, methyl ethyl ketone; alcohols, for example, FA or glycol (G); esters; ethers, for example, tetrahydrofuran (THF) or dioxane; or mixtures thereof.

Other additives known in the polymer art such as those defined above may also
30 be included in the polymer, polymer composite and/or mesophase carbon mixture. In

a preferred embodiment, the mesophase carbon is combined with a solution of novolac/HMTA/FA.

The binder phase may be mixed with the mesophase carbon in step (a) of the method of the invention using any suitable known apparatus, such as, for example, an Eirich mixer. The mixture of the binder phase and the mesophase carbon is generally cured at temperatures up to about 205°C under pressure, preferably about 1atm in step (b). The cured mixture is then heated or pyrolysed in step (c) up to temperatures of about 2000°C, preferably about 1000 to about 1500°C.

The carbon-containing material of the present invention has many desirable properties including controlled surface area, high density, good mechanical strength, Strain to Failure (StF) values and anti-corrosion properties. For example, the carbon-containing material may have a total surface area of 20 m²/g (Langmuir method) which gives excellent anti-corrosion, a high mechanical strength of about 60 MPa after curing and about 58 MPa after heating, a high carbon density of more than about 1.4 g/cm³ and improved oxidation resistance with the oxidation temperature under O₂ being higher than about 570°C.

These desirable properties enable the carbon-containing material of the present invention to have various industrial applications. High performance carbon materials having anti-corrosion properties are often required by the refractory industry to form cathodes in aluminium reduction cells or bricks in steel making vessels. On the other hand, good mechanical and anti-oxidation properties of carbon materials are important in the products used in steel processing.

Thus, the present invention also extends to articles manufactured from the carbon-containing material, for example, steel fabrication equipment such as slide gates or valves, tap hole blockers and blast furnace linings, electrolytic cells used in aluminium production and other engineering products such as thermal protection barriers, aerospace components and aircraft, satellite and space craft structures.

The method used to prepare the carbon-containing material of the present invention is simple and the precursors of the binder phase and the mesophase carbon are commercially available and cheap. Accordingly, the present invention has the

capability of producing a high performance material in an efficient and economical way.

The invention will now be described with reference to the following examples. These examples are not to be construed as limiting the invention in any way.

5 In the examples, reference will be made to the accompanying drawings in which:

Figure 1 is a graph showing a comparison between the surface areas of carbon materials containing mesophase and carbon black;

10 Figure 2 is a graph showing a comparison between the densities of carbon materials containing mesophase and carbon black;

Figure 3 is two graphs showing a comparison between the maximum strain of carbon materials containing mesophase and carbon black after (a) curing and (b) heating;

15 Figure 4 is six scanning electron microscope (SEM) images of composites having resin and (a)-(c) carbon black and (d)-(f) mesophase;

Figure 5 is three graphs showing (a) pore size distribution of carbon made from 100% polymer after pyrolysis to 1000°C, (b) pore size distribution of carbon made from 50% CB in polymer after pyrolysis to 1000°C and (c) pore size distribution of carbon made from 50% MPN in polymer after pyrolysis to 1000°C;

20 Figure 6 is a graph comparing carbon densities from composites made using an additive of carbon black (CB) and mesophase (MPN);

Figure 7 is two graphs showing (a) surface areas of composites made with CB and MPN as additives after pyrolysis to 1000°C; composite 2 is the repeat sample of composite 1 and (b) surface areas of carbons in composites made with CB and MPN
25 as additives after pyrolysis to 1000°C; carbon 2 is the repeat sample of carbon 1; and

Figure 8 is two graphs showing (a) pore size distribution of a composite made with CB as an additive after pyrolysis to 1000°C and (b) pore size distribution of a composite made with MPN as an additive after pyrolysis to 1000°C.

EXAMPLE 1

A mesophase pitch synthesised from naphthalene by catalytic reduction with HF/BF_3 is pre-heated under constant argon flow (7 ml/min). The pre-heating program used was 50°C/h to 500°C, keeping at that temperature for 1 hour followed by further 50°C/h to 600°C. The pre-treated mesophase was then pulverised with a ball mill for 1 min into powder before being blended with novolac resin with HMTA as the crosslinker in the solvent FA. The ratio of novolac/HMTA/FA was 40/8/52. Various samples with different ratios of resin and mesophase were prepared using this method and subsequently cured in 1 atm of pressure under the following curing profile.

The samples were heated to 90°C for 6 h, then the temperature was increased at a rate of 3.7°C/h to 135°C, thereafter 12°C/h to 205°C and finally at 205°C for 4 h. The cured composites were then pyrolysed to 1000°C at a rate of 50°C/h under an argon flow at 7 ml/min. The carbon-containing material produced was subsequently pulverised into a grain before various property tests were conducted.

Figure 1 shows the surface area of these carbon samples compared with samples prepared using the same methods, but where the mesophase was replaced by carbon black (CB). The surface area was obtained by measuring with N_2 at 77 K using a Langmuir Equation. The results show that, unlike the carbon black as a filler, the mesophase/resin system produces a low porosity carbon-containing material.

EXAMPLE 2

The pre-treated mesophase obtained in Example 1 was mixed with a novolac/HMTA (40/8 in ratio) resin powder in various amounts. 1 g of each mixed sample was then cold moulded into a block having the dimensions of 13 mm in diameter and 5-6 mm in thickness. The pressure used in moulding was 400 kg/cm². The blocks were firstly cured using the curing profile described in Example 1 and then carbonised to 1000°C at a rate of 50°C/h under argon flow. The bulk densities of the blocks after moulding, curing and carbonisation were calculated by measuring their dimension and weight.

Figure 2 shows that final carbon densities are higher with resins blended with mesophase compared to those blended with carbon black produced in the same way.

Such high density results in a high strength in the mechanical tests as shown in Figures 3a and 3b. After curing, the maximum strain of the blocks were similar in the range of additive to about 70 to 90% with both mesophase and carbon black derived blocks. However, pyrolysed blocks in the same range have a much higher maximum strain when mesophase is blended with the resin. The carbon black blended carbon material has a poor mechanical strength after pyrolysis.

The surface area measurement of the samples pulverised from the blocks resulted in the similar effects observed in Example 1.

EXAMPLE 3

The effect of carbon material derived from other sources, but not mesophase were also tested with a novolac resin. The novolac/HMTA/FA system described in Example 1 was blended with 50% of carbon powder pulverised from other carbon sources. These carbon sources include pulverised graphite, carbon obtained from the pyrolysis of pure novolac/HMTA/FA to 1000°C and carbon of the same pure resin after pre-treatment using the profile described in Example 1. The resulting mixtures were then cured and pyrolysed to 1000°C as described in Example 1. Table 1 shows that these carbon sources have similar effects to carbon black on the porosity of the final formed carbon/carbon composite.

Different types of mesophase were tested under the same conditions and the results are shown in Table 1 below. The other mesophase carbons used were mesophase derived from naphthalene without pre-treatment and mesophase derived from pitch with about 75% anisotropy. Table 1 indicates that these mesophase carbons have a similar effect on the porosity of the final formed carbon materials as pre-treated mesophase. The pyrolysis weight loss is also much higher.

Table 1. Effect of other carbon fillers on the carbon material formation from a novolac/HMTA/FA mixed system

	50% Carbon Black	50% pre-treated mesophase	50% graphite	50% resin carbon	50% pre-treated resin	50% un-treated mesophase	50% pitch mesophase
Cure Weight Loss (%)	11	12	10	19	12	11	13
Pyrolysis Weight Loss (%)	18	25	19	25	21	35	27
Surface Area(m ² /g)	266	33	46	266	215	12	17

5 EXAMPLE 4

The novolac/HMTA/FA system described in Example 1 was blended with 50% carbon black or 50% treated mesophase powder pulverized by a ball mill method. The composites formed with this method were then cured and pyrolysed to 1000°C as described in Example 1 being subjected to scanning electron microscopy (SEM) as shown in Figure 4. Figures 4a to 4c are the SEM images of the composite having 50% carbon black resin with different amplification. Figures 4d to 4f are the equivalent images of the composite having 50% mesophase and resin. As shown in the figures, the images with resin/carbon black composites appears as a non-homogeneous form where the carbon black powder can be clearly identified. On the other hand, the image of the block from the resin/mesophase composite gives a uniform material, indicating a strong interaction between resin and mesophase during curing and pyrolysis.

EXAMPLE 5

The novolac/HMTA/FA system described in Example 1 was blended with the powder of 50% carbon black (CB) or 50% mesophase (MPN), respectively. These powders were made by pulverization within a ball mill. The formed composites, together with pure resin, were cured and pyrolysed to 1000°C as described in Example 1. The resultant carbon and carbon composites were degassed under an argon flow at

400°C for 48 hours followed by full isotherm adsorption measurements with nitrogen at 77 K using a ASAP 2010 surface analyzer. A DFT plus software supplied with the analyzer then calculated the measured full isotherm curves to provide the pore size distributions. Figure 5 shows the pore size distributions calculated from these tested 5 samples.

The carbons derived from pure resin polymer gave a low surface area of 21 m²/g and no significant micropores appeared in the distribution, as shown in Figure 5(a). However, when 50% carbon black was mixed with the resin, the measured surface area increased to 266 m²/g as shown in Table 1 below and this 10 porosity is mainly contributed by micropores (8-10 Å pore width, Figure 5(b)). Assuming that the low surface area carbon black (~10 m²/g) did not become porous during the pyrolysis based on the results in Figure 1, the huge porosity from the composites with CB was obviously due to the effect of adding carbon black to the resin polymer during its carbonization. When 50% MPN was used, these additives 15 did not create any significant micropores in the carbons derived from polymer (Figure 5(c)). Therefore, using MPN to replace CB as an additive in the composite could avoid the formation of micropores in carbon derived from polymer.

Table 1. Effect of other carbon fillers on the carbon formation from novolac/HMTA/FA mixed system

	50 % Carbon Black	50% pre- treated mesoph ase	50 % graphite	50 % resin carbon	50 % pre- treated resin	50 % un- treated mesoph ase	50% pitch mesoph ase
Cure Weight Loss(%)	11	12	10	19	12	11	13
Pyrolysis Weight Loss (%)	18	25	19	25	21	35	27
Surface Area (m ² /g)	266	33	46	266	215	12	17

20

EXAMPLE 6

Two types of cement were formed by mixing of 24% of novolac, 34% of furfuryl alcohol, 4.6% of HMTA and 37.4% of two different additives: carbon black and mesophase, respectively. 6.5% of each of these two cements was then mixed,

respectively, with 38.5% of fine titanium diboride (TiB_2) and 55% of coarse TiB_2 . Two batches of 5.1 kg of each mixture were then compacted in a vibroformer make a lab block of the size about 150 x 150 x 60 mm. The pressure used to compact the block was standard pressure of 200 psi x 50 followed by vibration forming at ~ 100 psi. The densities of the formed lab blocks and their saturation values are given in Table 2 below.

Table 2. Physical data of tested lab blocks after compaction and pyrolysis

Sample Name	CB1	CB2	MPN1	MPN2
Density after compaction (g/cm^3)	3.45	3.54	3.52	3.52
Saturation after compaction (%)	90.0	92.4	91.8	91.8
Shrinkage after pyrolysis (%)	0.03	-0.19	-0.35	-0.31
Weight Loss after pyrolysis (%)	1.95	1.95	2.27	2.30

These blocks were then cured to 205 °C in an oven, and pyrolysed to 1000 °C while the blocks were packed in petroleum coke. The total weight losses after pyrolysis were similar for both types of composites and there was no obvious size shrinkage observed from these blocks (Table 2). However, the density of the carbon composite made with MPN as an additive has a higher value of 3.44 g/cm^3 compared with the value of 3.38 g/cm^3 of the composite using carbon block as an additive (Figure 6).

15 **EXAMPLE 7**

Each of the 4 lab blocks of the carbon composites obtained in Example 6 was cut in half and then sectioned into 6 strength bars having a size of 25 x 30 x 150 mm. These bars were then subjected to a three points bend test. Table 3 below gives the results from these mechanical tests.

20

25

Table 3. Mechanical test results from 3 points bend test for the composites made using CB and MPN as additives

Samples	CB	MPN
Strength (MPa) (average of 8 bars from the center of the composite)	2.71	6.57
Young's Modulus (MPa) (average of 8 bars)	715	1630
Strain to Failure (StF) (%)	0.38	0.40

The results show that the composites made using MPN as an additive have double the mechanical strength of the composites using CB as an additive. This result is in agreement with the result of the composites formed by polymer/additive only system (Example 2). The Young's Modulus of MPN sample also increased from 715 to 1630 MPa compared to the CB sample. Although the Young's Modulus has increased, the Strain to Failure of MPN sample was not reduced. It actually increased from 0.38 % to 0.4 %, which increased the capability of anti-corrosion such as anti cracks due to sodium penetration.

EXAMPLE 8

The lab blocks of carbon composites obtained in Example 6 were cut into the standard size of 25 × 30 × 150 mm and then subjected to compression tests. Table 4 below shows the results of these tests.

Table 4. Mechanical test results from compression test for the composites made using CB and MPN as additives

Samples	CB	MPN
Strength (MPa) (average of 6 samples)	11.9	25.8
Young's Modulus (MPa) (average of 6 samples)	1057	1720

Similar to the observation in Example 7, the mechanical strength of the MPN sample is 2.5 times stronger than the sample of CB. The Young's Modulus also increased from 1057 to 1720 MPa.

EXAMPLE 9

The lab blocks of carbon composites obtained in Example 6 were pulverized into powder by a ball mill for 1 min. These powders were then degassed in an argon flow at 400 °C for 48 hours. The surface areas of these samples were then measured and the results are shown in Figure 7.

As shown in Figure 7(a), the surface area of the composite made with carbon black is three times more than the composite made with mesophase. This indicates that using MPN to replace CB as an additive reduced the porosity of the composite substantially. As both composites were made from the mixture of cement and TiB_2 , and as the latter does not contribute to the porosity of the composite, the surface area measured is mainly contributed by the carbon derived from cement in the composite. Therefore, by counting the weight loss which is exclusively due to the cement, the surface areas of the carbons in the composites were calculated and are shown in Figure 7(b). The differences between the two materials in both diagrams are similar. The cement surface area of the composite made with CB is about $35 \text{ m}^2/\text{g}$, which is lower than the similar cement pyrolysed without TiB_2 . In Figure 2 of Example 1, the surface area of the carbon composite made from polymer and 37 % CB after pyrolysis is about $200 \text{ m}^2/\text{g}$. The reduction of the surface area indicates that in the composite with TiB_2 , the carbon black effect, has been reduced. This is because there is fewer interactions between the polymer and CB due to large amount of TiB_2 in the composite system. On the other hand, MPN in the composite did not cause any increase of the porosity on the carbon derived from polymer and therefore produced a low porosity composite.

EXAMPLE 10

Two powder samples from composites made with CB and MPN, after degassing with Ar at 400 °C, were used to measure their pore size distributions by a full isotherm adsorption with nitrogen at 77 K as described in Example 5. Figure 8 gives the pore size distributions of these two composites generated from the full isotherm curves by using a DFT plus method.

It is shown in Figure 8 that the porosity of the composite made with CB as an additive is mainly due to the micropores at about 10-11 Å pore width. This is similar to the results observed in the system without TiB_2 (Example 5, Figure 5). When CB was replaced by MPN, the resultant composite does not contain a significant amount of micropores and

therefore gives the composite a much lower porosity.

Since modifications within the spirit and scope of the invention may be readily effected by persons skilled in the art, it is to be understood that the invention is not limited to the particular embodiment described, by way of example, hereinabove.

5

DATED: 23 March 1999

CARTER SMITH & BEADLE

Patent Attorneys for the Applicant:

THE UNIVERSITY OF MELBOURNE

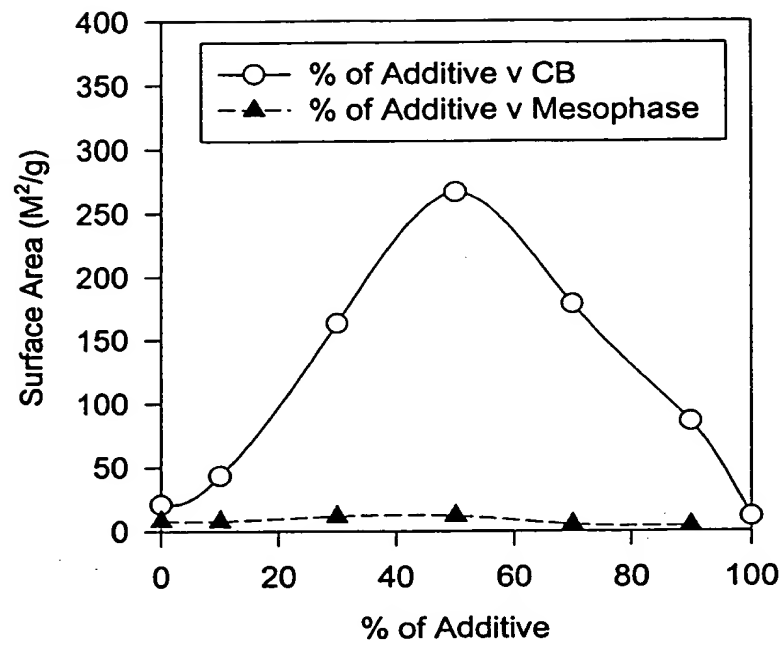


FIGURE 1

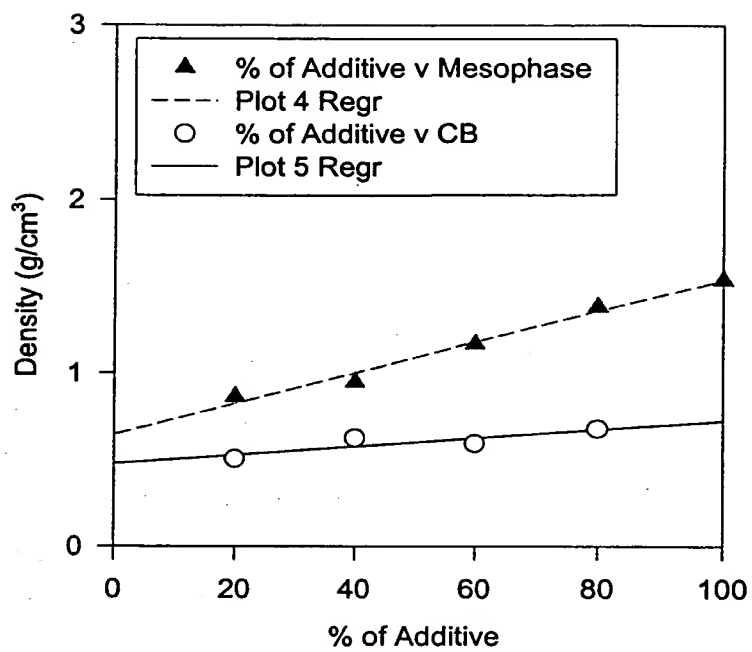


FIGURE 2

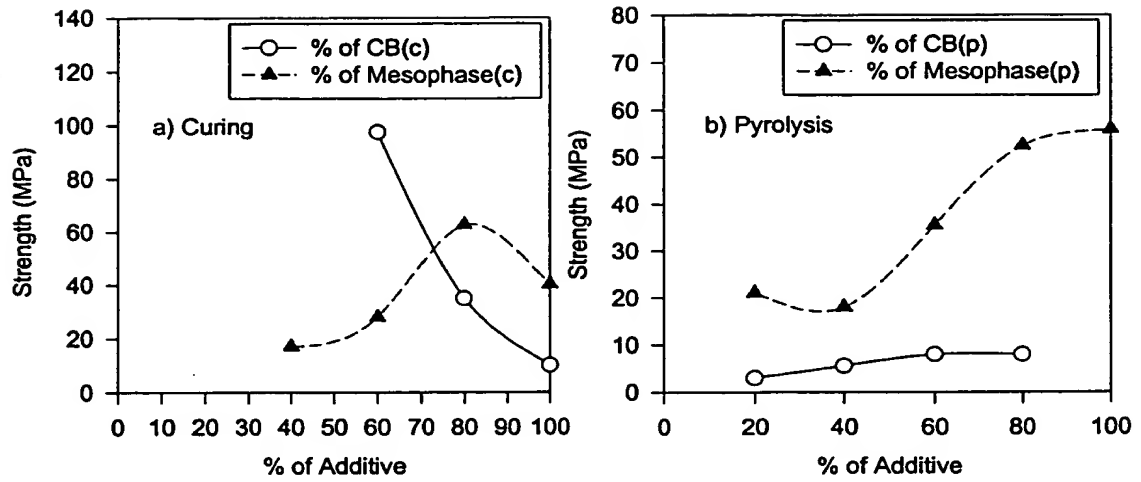


FIGURE 3

Figure 4a



Figure 4d



Figure 4b



Figure 4e



Figure 4c

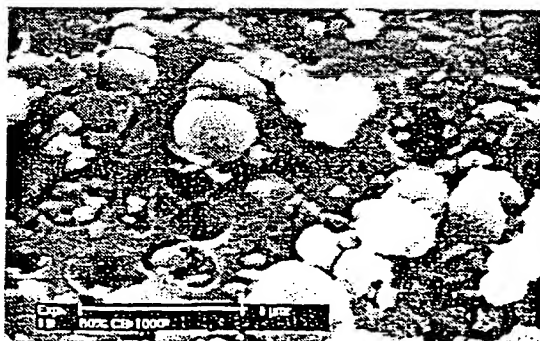


Figure 4f



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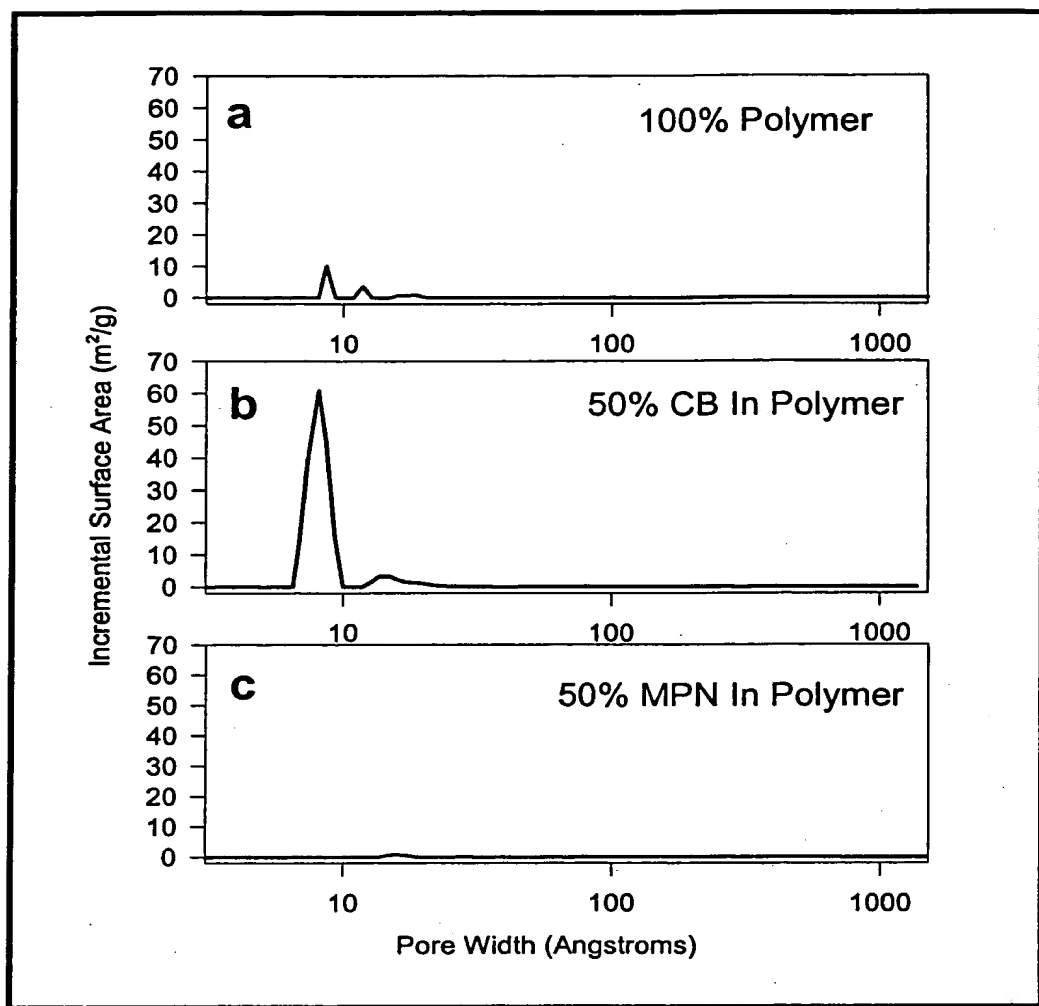


FIGURE 5

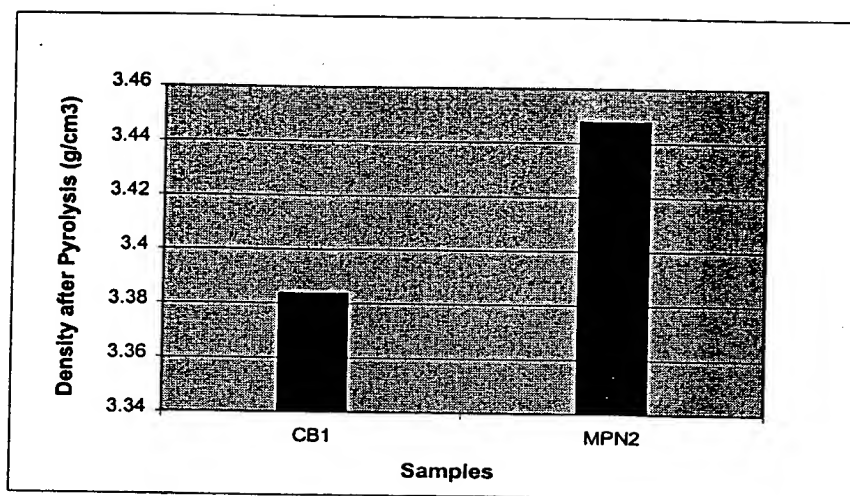


FIGURE 6

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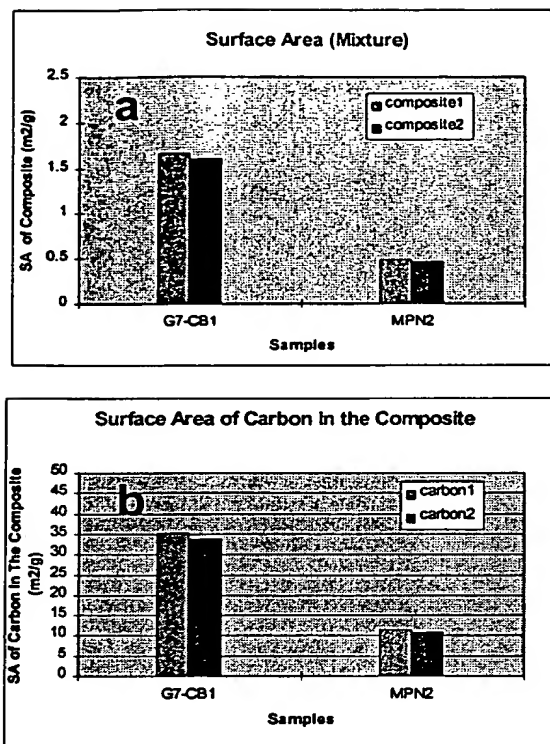


FIGURE 7

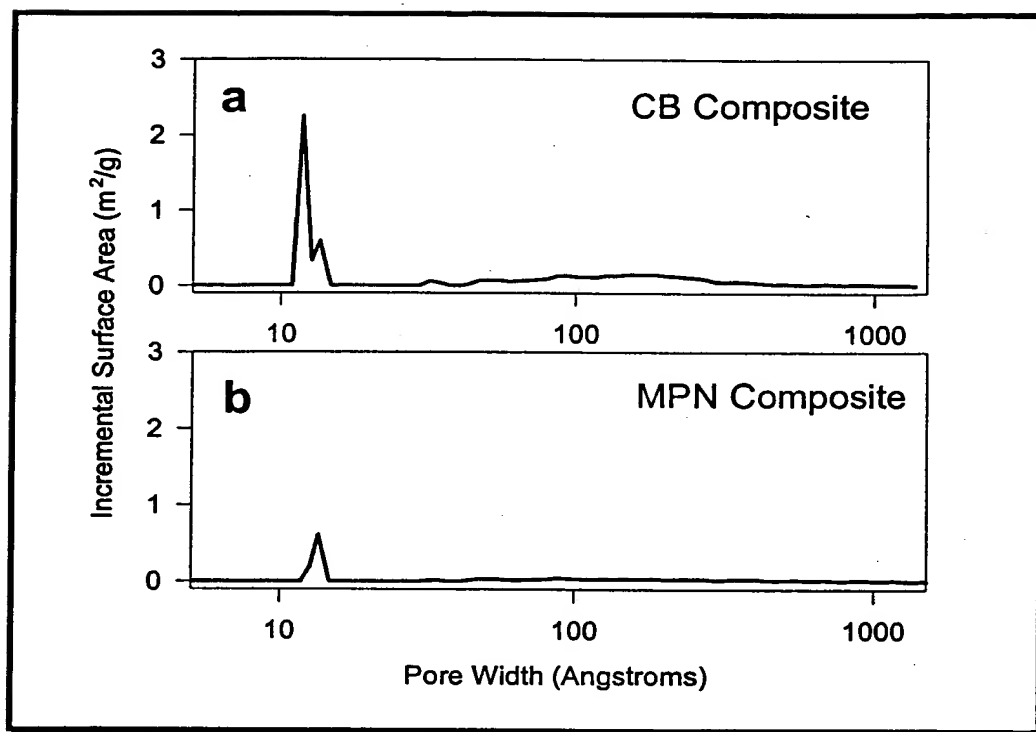


FIGURE 8